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The Use of Organic Reagents in Inorganic Analysis, With Applications to Qualitative Tests for Certain Metallic Ions

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THE USE OF ORGANIC REAGENTS IN INORGANIC ANALYSIS, WITH APPLICATIONS TO QUALITATIVE TESTS FOR CERTAIN METALLIC IONS

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The development of analytical methods utilizing the properties of organic compounds has been a somewhat recent advance, originating in large part with the use of dimethylglyoxime in 1905, and coming mostly during the last twenty years. These reagents, however, have been found in many cases to possess numerous advantages. Tests are often simpler, more rapid, more convenient and more accurate. Many reactions show a greater specificity and much higher sensitivity than inorganic reactions of the same ions. The great number of organic compounds provides a large source for the selection of suitable reagents, as well as the opportunity for synthesis of new materials to meet specific requirements.

This paper presents a survey of the theory and general principles of the organic reactions which have been found analytically useful. This is followed in Part II by detailed discussion of several qualitative tests for metallic ions with experimental results on sensitivity and interferences and consideration of the conditions under which the tests may be applied.

-I-

Processes in which organic reagents are utilized in analysis may be classified into several types.

(1) Of these types the most important and the most frequently met is that in which a metallic or non-metallic ion or molecule

combines with the molecule of the reagent by some mechanism to give a color reaction or a precipitate. Within this group are included combination by chemical forces (electronic forces) and by physical forces (extra-molecular forces). The chemical force may be either a normal valence bond or a coordinate bond, or combinations of both of these. Several authorities divide this whole general group into divisions corresponding to such particular types, but it seems best to treat all these methods of combination as one unit in order to emphasize two facts:

(a) There is no sharp distinguishing line between the various modes of combination, for they all are manifestations of the same atomic forces exercised in different ways. For example, the normal or primary valence bonds and the secondary or coordinate valence bonds appear to be interchangeable as far as effect on ring structure is concerned.

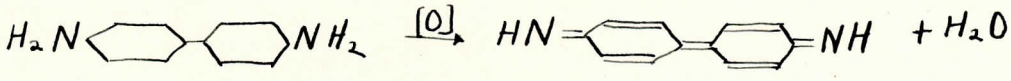
(b) Many of the compounds produced have not yet yielded accurate indication of their exact nature or composition, either because of experimental difficulties or because of insufficient study. Particular mechanisms are often the object of disagreement among authorities.

Classifications made too categorically by some authors are for these reasons not consistent and at the same time they fail to make clear the true nature of the distinctions which can be made.

(2) The oxidizing or reducing nature of the substance being tested for may be used to convert the reagent into a different organic compound, or the substance itself may be oxidized or

reduced by the organic reagent to a compound with distinctive properties.

Acetic acid solutions of benzidine are oxidized by higher metal oxides, certain oxidizing and autooxidizing substances, and certain easily reduced complex compounds, to give a blue meriquinoid compound:



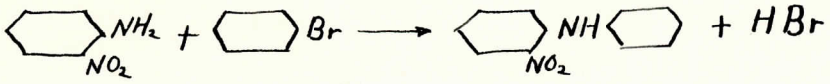
This is a very sensitive test for chromate ion, and is also used for manganese, cerium, lead, copper, thallium, phosphoric acid, cyanide, silicate, persulfate, and vanadate (12, 35). 2,7-diaminofluorene and tetramethyldiaminodiphenylmethane form similiar colored meriquinoid compounds.

Selenium may be identified by the oxidizing effect of selenium dioxide on organic compounds. Tin and vanadium may be identified by the reducing action of their lower valence states on cacotheline, a derivative of the complex organic substance brucine, giving a very sensitive test with a color change from yellow to violet (12).

One of the usual organic tests for reducing sugars may be reversed and used as a method of detecting copper. If the unknown solution is mixed with Rochelle salt and sodium hydroxide until a deep blue solution results and if this is boiled and glucose added, the presence of copper is indicated by a red precipitate of Cu_2O (8, p. 150).

(3) The inorganic substance may act as a catalyst in a reaction involving the organic reagent, or the organic substance may catalyze an inorganic reaction, in either case yielding a product with suitable distinctive properties.

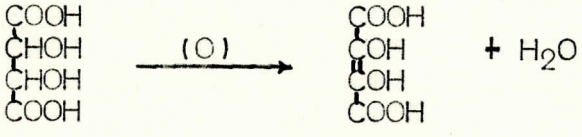
The reaction



is catalyzed by alkali iodides, affording an identification of iodide ion.

"The reaction $2NaN_3 + I_2 \longrightarrow 2NaI + 3N_2$ is accelerated by carbon disulfide, involving the intermediate action of sodium azidodithiocarbonate; this makes possible not only the very sensitive determination of carbon disulfide but also a direct iodometric determination of azides." (12)

Tartaric acid is catalytically oxidized to dihydroxymaleic acid by hydrogen peroxide in the presence of ferrous or copper ions; the two last may be identified by this means (35):



(4) The inorganic substance may enter directly into the synthesis of some organic compound by reacting with the organic reagent. This differs from type (1) in that the nature of one or both of the reactants is drastically changed, and the inorganic substance concerned is usually a polyatomic anion.

For example, nitrates are colorimetrically estimated by the formation of methyl orange with dimethylaniline and sulfanilic acid in acid solution; the red color produced is also suitable for a spot test (16).

Hydrogen sulfide is identified by the formation of methylene blue from p-aminodimethylaniline and ferric chloride (24).

Bromide is tested for by reacting it with fluorescein to form red tetrabromofluorescein (eosin); chloride does not interfere but iodide gives the same result (35).

Nitrous acid may be detected or determined by the method of Greiss long in use: sulfanilic acid is diazotized by the nitrous acid and then coupled with a-naphthylamine to yield color (12).

(5) The organic compound may act as an indicator in an inorganic reaction. This is, of course, a use long known and widely applied.

(6) Organic compounds may be used to control conditions in order to direct the course of a reaction involving other substances.

They are used for control of concentration of inorganic reactants, especially to reduce ion concentration below the precipitation point. Alkali salts of organic acids, such as acetic, control pH. Precipitation of heavy metals as hydroxides is prevented by alkali salts of hydroxy acids and by polyhydroxy compounds such as tartrate, citrate, glycerol, mannite and various sugars. These organic substances form extremely stable complexes with such metallic ions as iron, aluminum and chromium.

Caldwell and Moyer (5) give a method for completely separating zinc from cobalt by precipitation with hydrogen sulfide with use of certain aldehydes, most effective of which is acrolein. These serve to reduce the hydrogen sulfide on the surface of the zinc sulfide particles, reducing post-precipitation since the concentration falls below the precipitation value. It is supposed that hydrogen sulfide "will react with aldehydes under the above conditions to give various types of polymerized thioaldehydes."

Ostroumov uses pyridine and the pyridine salt of hydrochloric acid to precipitate cobalt and nickel in a crystalline state and separate them quantitatively from manganese in one precipitation with hydrogen sulfide (26).

Cyanide ion shows special properties which can be made use of in inhibiting the reaction of certain metals.

Benzidine, O-toluidine, and related compounds are used in the dimethylglyoxime test for cobalt to intensify the color and increase the sensitivity. The mechanism does not seem to be explained.

(7) The solvent nature of organic substances may be used. Organic solvents may serve as vehicles for reagents. Water-immiscible solvents, on the other hand, are applied in extraction to remove interferences or to make a test more sensitive, as by separation of metals by extraction with chloroform or carbon tetrachloride in the dithizone determination (18), or by concentration at a liquid interface in the chloroform flotation process for aluminum with aluminon, respectively.

(8) Organic substances are used in colorimetric determinations to prepare stable suspensions--colloidal dispersions--of insoluble metal salts or similiar materials.

Such substances as gelatin, egg albumin, dextrin, and gum arabic may be used as peptizing agents. Feigl also indicates (12) the possibility of the use of the "water-soluble cellulose ethers" for this purpose.

Type (1) has not only shown the most rapid recent development and greatest promise for future advance, but it represents in large part a new aspect in the development of our knowledge of chemical

affinity, to be specific, in the study of complex formation and chelation. Therefore it will be discussed in further detail.

Let us first consider those examples of combination which are, or are thought to be, essentially chemical in nature. Now it is possible for metals to add on to organic molecules in two ways.

The first is by replacement, by one equivalent of metal, of hydrogen in an acidic group, such as one of the following:

Primary amine	$-NH_2$	Mercapto	$-SH$
Secondary amine	$-NHR$	Oxime	$=NOH$
Carboxyl	$-COOH$	Sulfinic	$-SO_2H$
Hydroxyl	$-OH$	Sulfonic	$-SO_3H$
Enolic hydroxyl	$-OH$	Imino	$=NH$

Beside compounds containing these groups, there are included compounds which may form one of them upon molecular rearrangement.

The second method of addition is by a coordination bond, that is by the saturation of residual valence of a metal by an atomic group containing an atom such as nitrogen, sulfur, or oxygen, without replacement of hydrogen. Groups capable of doing this include:

Alcoholic hydroxyl	$-OH$	Cyclic tertiary amine	$=N-$
Primary amine	$-NH_2$	Carbonyl	$=O$
Secondary amine	$-NH-$	Oxime	$=NOH$
Tertiary amine	$-\overset{\displaystyle |}{N}-$	Thioether	$-S-$

These atomic groups have electrons which are not in action as valence electrons, and are able to give electron pairs to metallic ions to bring the latter up to a stable electronic structure. After exchange of electrons, there seems to be no difference in the resulting bond from that of normal covalence.

If an organic molecule contains two, or more, of these groups capable of joining with a metallic atom, either both acidic, or both coordinating, or, by far the most common, one of each, and if these groups are in the proper structural relationship with one another, then there is possible the formation of a ring between a metal and the the organic molecule. A substance having a ring of this nature is known as a chelate compound.

The strain theory of Baeyer seems applicable to the formation of chelate rings. Those most stable contain six members and two double bonds, or five members and no double bonds. Most rings contain five or six atoms, a few are stable with four members, while those of three or of more than six members are very rare.

"The nature of the non-metallic atoms in the ring appears to be unimportant, but theyaare most frequently carbon, nitrogen, oxygen, or sulfur. The metal is almost always ~~always~~ attached to a nitrogen, oxygen or sulfur atom by a normal covalence, very rarely directly to carbon. The ring is usually closed by means of coordinate valence from the metal to a nitrogen, oxygen, or sulfur atom, rarely to carbon; however, it may also be closed by another normal covalence. In rare cases two coordinate valences may complete a ring." (29).

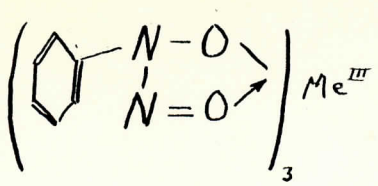
Chelate rings which are non-electrolytes are termed by Diehl "inner complex" compounds. These are frequently very stable and often intensely colored. They "have very unusual properties; because of their non-polar character they are insoluble in ionizing solvents but soluble in non-ionizing solvents; they have low melting and boiling points or sublime readily; they are highly stable and with one notable exception never occur with water of crystallization;

their color depends on the structure of the molecule and departs widely from that of normal salts of the metal." (10, p.9). It is these properties which make them desirable in analytical reactions, both qualitative and quantitative.

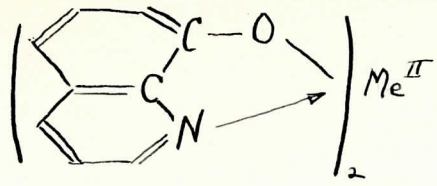
There are several classifications of the types of chelate compounds. Diehl classifies them according to the number of groups which combine with the metal, with subdivisions as the groups are respectively acidic or coordinating.

Haendler and Geyer have listed the reagent types by the atoms connecting the two functional groups, followed by the structure of the functional groups themselves, each in alphabetical order, as given below. This arrangement requires no knowledge of the acidic or coordinating nature of the bond-formation in the resulting metal complex. Structural formulas of complexes of several of the examples are given for illustration. (24, p.3)

C-N,SH	Mercaptobenzothiozol
C-NH,SH	Rubeanic acid
C-NOH,OH	Benzohydroxamic acid
N-NONH_4,O	Cupferron (A)
C,C-N,NOH	Phenyl-a-pyridyl ketoxime
C,C-N,OH	8-Quinolinol (B)
C,C-N,SH	8-Quinolinethiol
C,C-NH,SH	Thionalide
C,C-NH_2,OH	Glycocoll
C,C-NOH,NOH	Dimethylglyoxime (C)
C,C-NOH,O	a-Nitroso-b-naphthol
C,C-O,OH	Oxalic acid
C,C-O,SH	Thioglycolic acid
C,C-OH,OH	Catechol
C,C-OH,SOH	Thiohydantoic acid
C,N-NH,NOH	Nitrosoguanidine
C,N-NH_2,OH	Hydrazinecarboxylic acid
C,N-NH_2,SH	Dithizone (D)
C,C,C-N,NH	Chlorophyll type
C,C,C-NOH,OH	Salicylaldoxime (E)
C,C,C-O,OH	Alizarin
C,C,N-N,NH	Phthalocyanine
C,C,N-NH,NH	Biguanidine
C,C,N-NH,NH_2	Biuret
C,C,N-NH,O	Dicyandiamidine (F)



(A)



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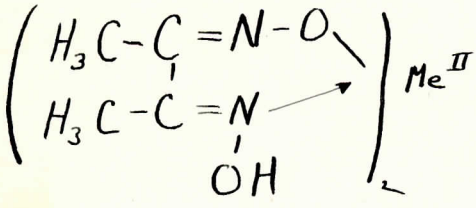

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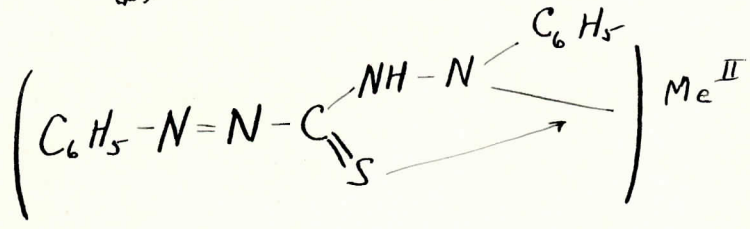
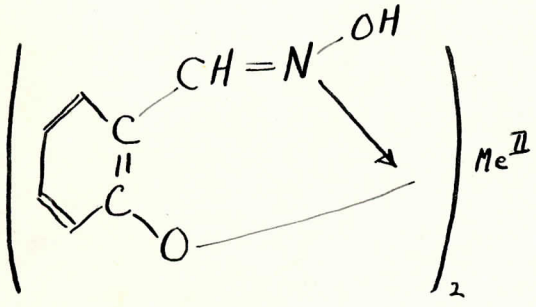
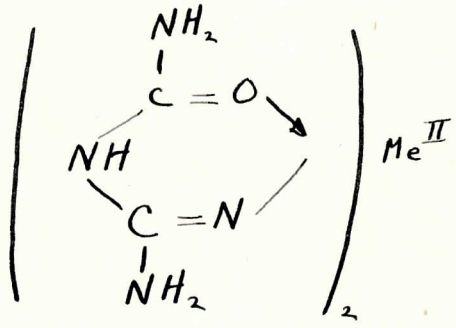


(D)



(E)

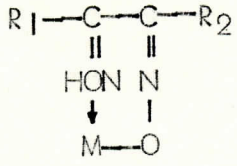


(F)

We will now proceed, with the aid of a rough generalized classification based on the principal functioning group, to examine typical examples of various sorts of organic molecules which add metals. The most common kind of chelating compound--those molecules which add with one normal valence and one coordinate valence--is presented first. Following this are listed some addition products wholly the result of coordinate valence, and then a few normal salts.

Oxime Group-

The dioximes have the general formula $R_1-C(:NOH)-C(:NOH)-R_2$. The alpha-dioximes react with several metals to form chelate rings; in these the hydrogen of one oxime group is replaced while the metal is held by coordination to the other group:

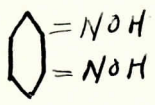


Dimethylglyoxime and other o-dioximes yield red precipitates with nickel salts in basic solution and yellow precipitates with palladium in acid solution and no other precipitates. These metals may be quantitatively separated from each other by control of acidity. Pink to red soluble compounds are formed with ferrous iron, purple with copper, yellow with bismuth, reddish brown with cobalt.

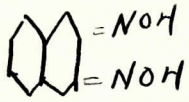
Other important dioximes are benzildioxime, furildioxime, and cyclohexanedionedioxime, all specific for nickel. Benzildioxime is more sensitive than dimethyl- quantitatively, but because of its own insolubility in water is likely to be precipitated ($C_6H_5-C:NOH-C:NOH-C_6H_5$). Furildioxime ($C_4H_3O-C:NOH-C:NOH-C_4H_3O$) combines the advantages of high molecular weight, solubility in water, and low solubility of the nickel derivative. Cyclohexanedionedioxime is soluble in water and quite satisfactory qualitatively; its quantitative relations have not been thoroughly investigated because of the unavailability of the reagent (10).

It is seen from the fact that o-benzoquinonedioxime and o-naphthoquinonedioxime have no power of selective reaction but

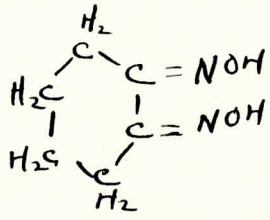
give brownish precipitates with most metals, that while the functional groups are the oxime groups, the remainder of the molecule exerts a conditioning influence, for when the double bonds are saturated as in cyclohexanedionedioxime, specificity returns. From this it seems that R_1 and R_2 must be in a certain degree of saturation for the formation of chelate compounds; otherwise the dioxime reactions are those of a dibasic acid (24).



o-benzoquinone dioxime



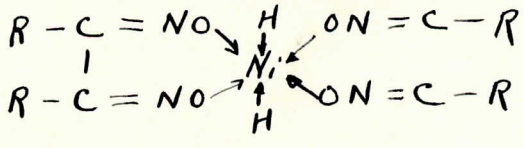
o-naphthoquinone-dioxime



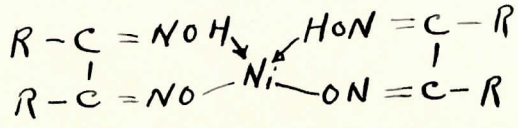
cyclohexane-dionedioxime

There are three stereoisomeric forms of the symmetrical dioximes, known as the alpha, beta, and gamma forms. The alpha form is the one which enters into the common metal reactions; the beta form is completely unable to react with metals; the gamma form gives yellow compounds with nickel, rather unstable, in which both hydrogens are acidic. It is now believed that the alpha form represents the anti- structure, beta, the syn- structure, and gamma, the amphi- structure. Thus the nitrogens must be free in the the direction towards one another in order to produce the common reactions.

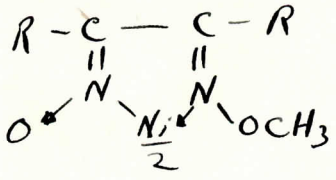
According to Lowry(24) the complex structure is:



and, according to Feigl (12):

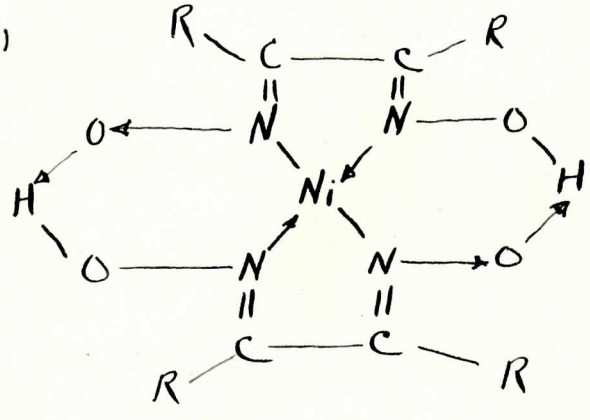


The structure of these complexes is indicated by analogy with the similiar nickel rings of certain closely related compounds. The complex of the mono-O-ether of benzildioxime show that one OH group is not involved:



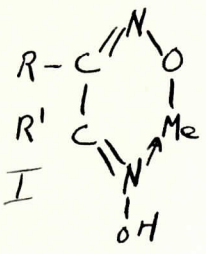
This is also shown by the fact that an imino group serves as well as one of the oxime groups.

There is also now apparent in the Feigl structure the possibility of isomerism, depending upon whether the coordination bonds are adjacent or opposite. The failure to observe such isomerism is explained by Diehl with the following formula which is also supported by the lack of reactivity of the hydroxyl group of the complex: (10)

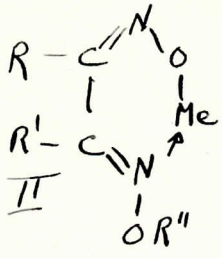


Considering the oximes more generally with the aid of the following formulas, we find that either alkyl or aryl groups may replace the R, R', or R'' in formulas (I), (II), and (III) and the compound may be either symmetrical or unsymmetrical. The hydrogen of one of the oxime groups may be replaced by an organic radical or the entire group may be replaced by an imino group without losing characteristic nickel precipitating properties, while the nitrogen

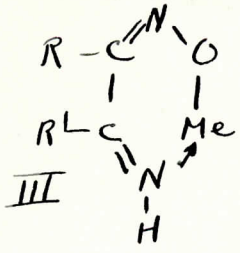
of a pyridine ring maintains the same activity. Formula (V), 2-pyridylformaldoxime, represents the condition in which one carbon atom is part of an unsaturated ring, while (IV) shows the nickel salt of nitrosoguanidine which has three nitrogens and one carbon. All of these act as monobasic acids. (29)



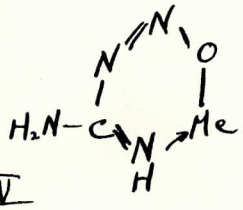
I



II

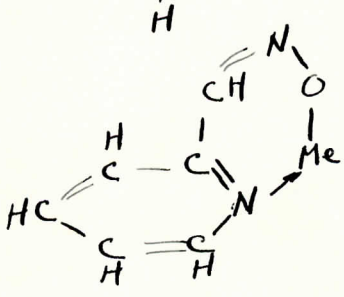


III



IV

V

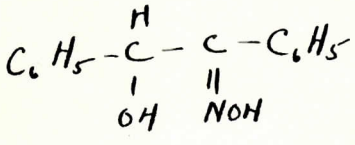


Oximino alcohol compounds have an oxime group plus a hydroxyl group. The class of oximino alcohols can be subdivided as the hydrogen in both groups is replaced, or as it is replaced only in the hydroxyl group.

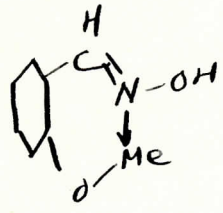
a-Benzoinoxime and its analogs form complexes in which such metals as copper take out two hydrogens to form a six-membered ring with one double bond, wholly by normal covalence. Salicylaldoxime and its analogs yield complexes in which the hydrogen of the hydroxyl group is replaced and the oxime group coordinates with the metal, giving a six-membered ring with two double bonds, insoluble in dilute acid.

The copper complexes of the o-hydroxy oximes usually are insoluble in water; their solubility in ammonia appears to depend upon whether the remainder of the molecule is capable of satisfying

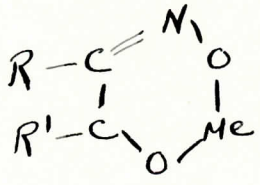
the coordination valences of the metal: aromatic radicals, amino groups, and alkyl groups of four or more carbons give insolubility. Cyclohexanoloxime gives a green water-insoluble copper salt which is soluble in ammonia. 2-pyrrolealdoxime, with the oxygen of the hydroxyl group replaced by nitrogen, also gives an insoluble copper complex(29):



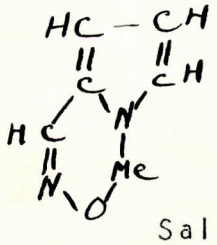
Benzoinoxime



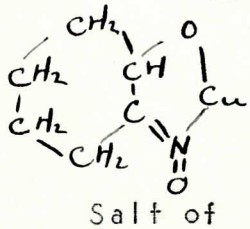
Salt of salicyl-aldoxime



Salt of an acyloin oxime



Salt of 2-Pyrrolealdoxime



Salt of Cyclohexanoloxime

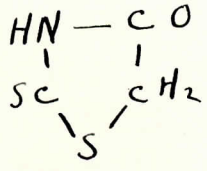
The oximino ketones have neighboring oxime and keto groups. The most important type is a-nitroso-b-naphthol, together with the closely related nitroso-R-salt and 2-isonitroso-1-ketotetralin. These may be considered also to have enolic hydroxylic groupings together with nitroso groups and they will be discussed under this classification.

Imino Group-

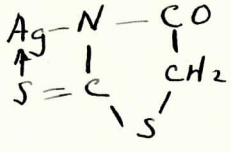
The hydrogen of the imino group is very active and replaceable by a metal. Rhodanine and its derivatives, containing this group, generally form yellow precipitates with Cu, Au, Hg, Pt, Ag, and Pd ions in acid solutions. Cyanide inhibits the precipitation of gold and mercury. Silver is frequnetly tested for by this means and forms a four-membered chelate ring with one double bond (24).

Since the hydrogen atoms in the CH_2 group are very active, rhodanine may be condensed with many aldehydes wnd ketons, and the derivatives have the same precipitating properties as the parent substance. 5-(p-dimethylaminobenzal)rhodanine, which gives a reddish-violet precipitate with silver is a good example of the improvement of the characteristics of a reagent by substitution, in this case by the introduction of a chromophoric group. This test is sensitive to one part in 5,000,000.

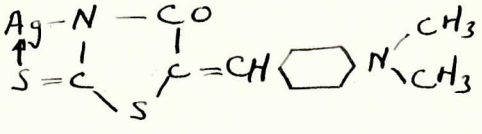
5-(p-dimethylaminobenzal)rhodanine has the disadvantage for quantitative work that it is insoluble in water and is partially thrown down in aqueous solution; this difficulty may be overcome by sulfonation of the molecule which makes it water-soluble (12, 24).



Rhodanine

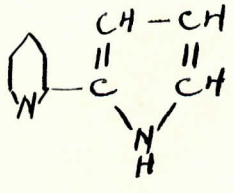


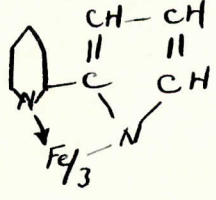
Silver complex



Silver complex of 5-(p-dimethyl-aminobenzal)rhodanine.

In the rhodanine derivatives, imino acidic hydrogen is replaced by the metal which then coordinates with an atom of sulfur (Feigl calls the rhodanine addition products normal salts but gives no evidence). On the other hand 2-(2'-pyridyl)pyrolle forms complexes in which the metal coordinates with a nitrogen atom and replaces an imino hydrogen to form a five-membered ring. Copper, cobalt, nickel, and ferrous ions react (24, 29).

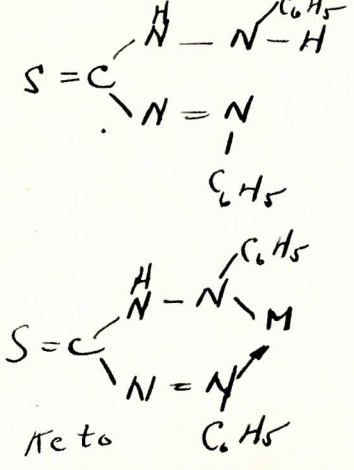




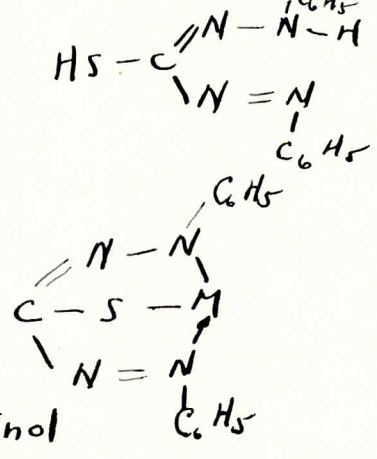
Mercapto Group-

The mercapto group contains an extremely active acidic hydrogen, easily replaceable by a metal. The commonly used reagents containing this group give five-membered rings with no double bonds.

Dithizone (diphenylthiocarbazone) reacts with many metals to form complexes. This reagent undergoes tautomeric shift, existing in an enol form and in a keto form. In a neutral or acid medium there are produced derivatives of the keto form, which are insoluble in water, but produce intensely colored solutions with organic solvents. Derivatives of the enol form are insoluble in both. Dithizone is not specific in reaction, but it is extensively used under controlled conditions for many very convenient and sensitive qualitative tests (24, p.16):



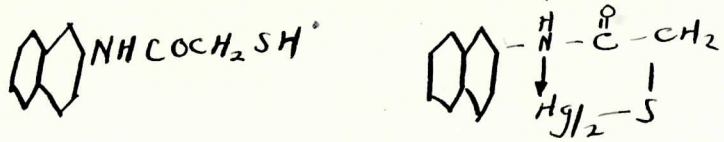
Keto



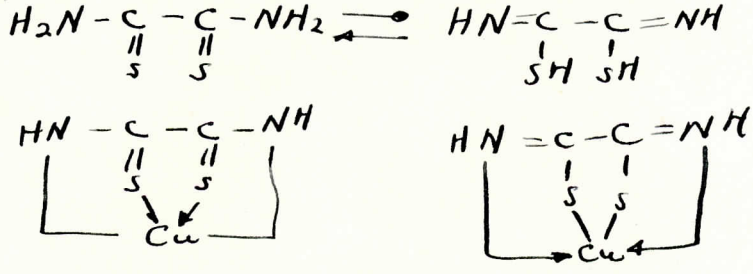
Enol

Thionalide (thioglycollic acid b-aminonaphthalide), like other derivatives of thioglycollic acid, acts in neutral solution as a derivative of hydrogen sulfide, precipitating the characteristic heavy metals of the sulfide ion, but with much greater sensitivity. Characteristic colors of sulfide precipitates are not carried over, however. Specificity can be gained by control

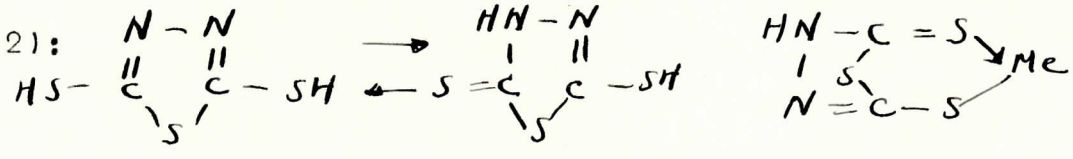
of conditions, as by precipitation from mineral acid solution or in the presence of tartrate or cyanide (12).



Rubeanic acid, the diamide of dithioxalic acid, exists in tautomeric forms. It reacts with nickel, cobalt, and copper to produce insoluble complexes, precipitated quantitatively from strongly ammoniacal solution. This is explained bythe fact that the equilibrium is shifted to the precipitating diimido form of the reagent when the hydrogen ion concentration is low. However, the precipitates when once formed are insoluble in dilute mineral acid. Cyanide inhibits the reaction, forming more stable complexes.

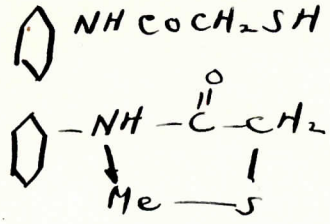


2,5-dimercaptothiodiazol reacts with many metals in the mercapto form; the bismuth complex exhibits a specificity of color, being deep red in contrast to white to yellow for other metals (12):

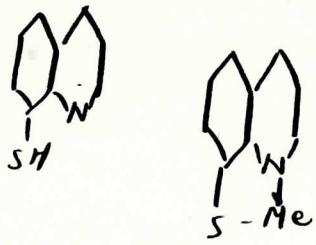


Mercaptoacetanilide (thioglycollic acidanilide) and mercaptoquinoline are other complex-forming compounds with an acidic

hydrogen in an SH group (29).



Mercaptoacetanilide



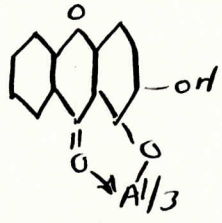
8-Mercaptoquinoline

Hydroxyl Group-

There are two sorts of these reagents: those containing the ordinary hydroxyl group and those with an enolic hydroxyl group.

Of those reagents containing the ordinary hydroxyl group, the outstanding examples are the hydroxyanthraquinones, the hydroxyquinolines, and the derivatives of arsonic acid, together with some compounds containing an oxime group as well, which were considered with the monoximes.

The hydroxyanthraquinones form chelate rings of six members and one double bond with Al, Ba, Be, Ca, Cr, Fe, Mg, Sr, Zr ions. Alizarin is used as a reagent for the detection of aluminum, forming a red precipitate:



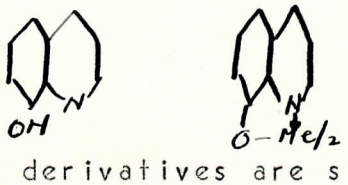
Feigl classifies this as an example of a reaction "in which they organic component possesses the character of a dyestuff," the resulting complex is accordingly called a color lake.

Alizarin sulfonic acid ("alizarin-S") is also used for this purpose. Quinalizarin(1,2,5,8-tetrahydroxyanthraquinone) lakes

are used in the detection and determination of beryllium and magnesium.

Liebhofsky and Winslow have studied the properties of the anthraquinones and evaluate them as very general and accurate metallic reagents, almost universally applicable for colorimetric determination of isolated ions, although some degree of specificity may be obtained by pH control (23).

Most used of the hydroxyquinolines is the 8-hydroxy- derivative, known as oxine, which reacts with many metals forming five-membered rings with no double bonds.



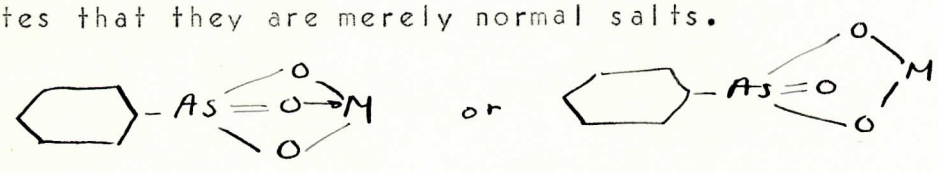
The metallic derivatives are suitable for drying and weighing. In addition volumetric determination is made possible through bromination to form 5,7-dibromo-8-hydroxyquinoline, and colorimetric determination by coupling with azo compounds in alkaline solution.

Boyd, Degering and Shreve have studied the reactions of a number of azo derivatives of oxine with metals (3). They found that while the substitution did not greatly change the properties of the reagent, its activity could be modified in details. For example, the substitution of groups para to the point of coupling in the aromatic nucleus which tend to increase the solubility of the compound in polar solvents gave a more positive reaction. They also found that while chloride ion interferes, tartrate, contrary to previous belief, usually does not.

The organic derivatives of arsenic acid are useful in analysis. Phenylarsenic acid precipitates zirconium, while thorium will then

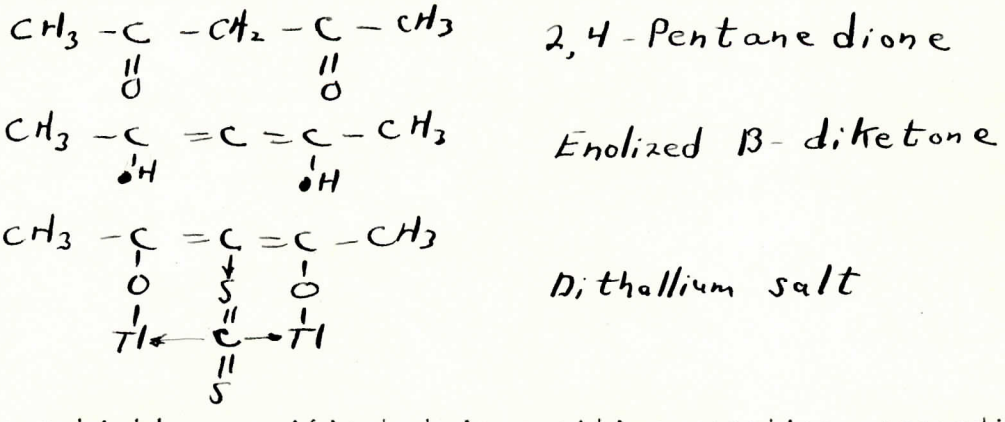
come down in solution buffered with acetate. N-propylarsenic acid also precipitates zirconium quantitatively, while p-n-butylphenylarsenic acid precipitates iron quantitatively. Chromophoric groups have been introduced, as in p-dimethylbenzeneazophenylarsenic acid which gives a sensitive spot reaction with zirconium (120.

Mellan and Sarver (24, 29) consider the complexes of these arsonic acids to have two four-membered rings, but the coordinate valence seems not to be definitely established, for Feigl (12) states that they are merely normal salts.



Phenylarsonic acid.

Compounds containing the enolic hydroxyl group are the tautomers of enolized ketones and diketones. Enolized b-diketone reacts with thallium in the presence of carbon disulfide to give a chelate ring of six members and two double bonds (24, p. 12)



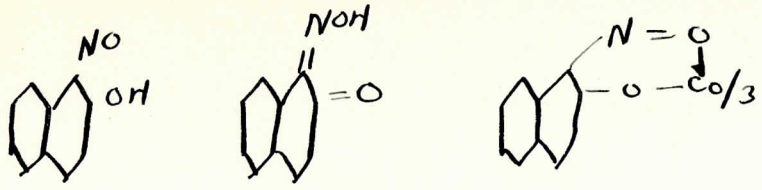
2,4-Pentanedione

Enolized β-diketone

Dithallium salt

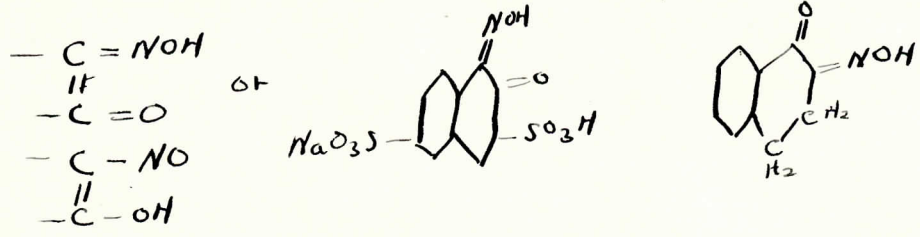
This is a highly specific but insensitive reaction, according to Sarver . If one ketone group only is enolizable, the CS_2 does not react, but a monothallium salt is formed (29).

a-Nitroso-b-naphthol is a monoxime with a keto group in a weakly acid medium, shifting to a phenol form in strongly acid medium (24, p. 13):



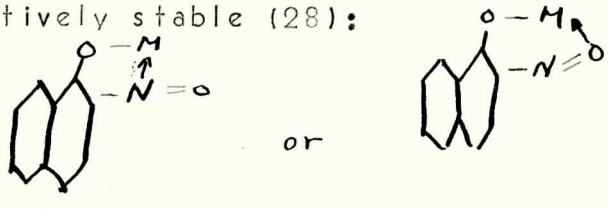
Enol Keto Cobalt complex

It forms colored metallic complexes with rings of six members and two double bonds. b-Nitroso-a-naphthol forms complexes with cobalt of similiar properties. The same reactive grouping is present in the molecules of nitroso-R-salt and 2-isonitroso-1-ketotetralin which behave similiarly toward cobalt:



The nitrosonaphthols precipitate iron and palladium, and in acid solution, zirconium. Oximino ketones generally react with ferrous ion to give deep blue soluble chelate compounds, with ferric to give green colors, and with cobalt to give red precipitates. The same behaviour is shown if the carbons are aliphatic, as in a-benzil monoxime, or they may form part of an incompletely saturated aromatic ring (29).

Another of these reagents, 2-nitroso-1-naphthol-4-sulfonic acid partially precipitates several metals, and gives beautiful red, orange, and green soluble complexes with Co, Cu, and Fe^{++} ion, which are relatively stable (28):



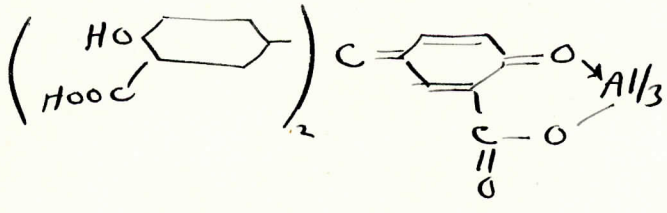
Isonitrosoacetone, diisonitrosoacetone, and isonitroso-acetophenone are oximino ketones thought to react as enols. They

form water-soluble colored compounds with ferrous ion; in the case of diisonitrosoacetone the reaction is inhibited by presence of cobalt, nickel or manganese (24).

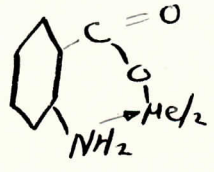
Analagous in structure are the complexes of "cupferron", the ammonium salt of nitrosophenylhydroxylamine, used originally for the separation of copper and iron from other metals, and since adapted for several other separations. Combination is with an NO group by coordination, while the NH_4 of an $NONH_4$ group is replaced (12).

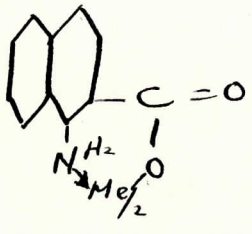
Carboxyl Group-

Aurintricarboxylic acid, usually used in the form of ammonium salt (aluminon), forms a red aluminum lake, suited for detection and colorimetric determination.



Anthranilic acid and quinaldinic acid are o-aminocarboxylic acids, forming complexes according to the formulas (12):

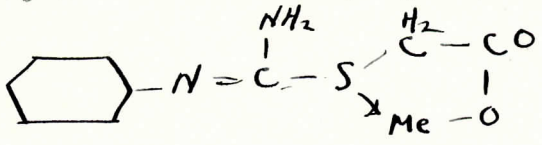




Anthranilic acid is used for the determination of divalent metals gravimetrically and by an indirect volumetric determination with bromine. Cu, Hg, Pd, Zn, and Ag ions form characteristic crystalline precipitates identifiable under a microscope. Cu, Cd, and Zn are gravimetrically determined with quinaldinic acid, but the pH ranges

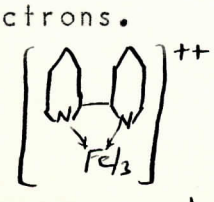
of precipitation overlap (31).

Phenylthiohydantoic acid, which precipitates cobalt in slightly ammoniacal solution and other metals in acid solution contains a sulfur group available for ring formation after the acidic hydrogen of the carboxyl group is replaced (37):

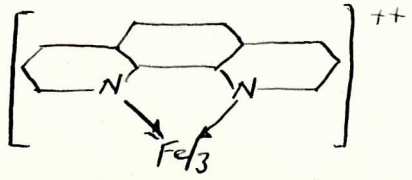


Compounds Formed Wholly by Coordinate Valence-

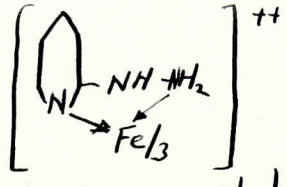
a,a'-Dipyridyl and a,a'-phenanthroline act with certain metals to form addition compounds; with ferrous salts there is produced an intensely red, water-soluble complex ion which is stable toward dilute acid and oxidation in the air. The complex contains three molecules of organic reagent for each ferrous ion, thus it is of the hexammine type with six nitrogen atoms coordinated with the iron atom. Other metals also combine with these reagents, but in acid solution Fe, Cu, Co, and Ni ions only give a color reaction (12). Feigl terms this an especially sensitive method of detecting traces of ferrous salts. Sarver (29) states that these complexes when taken in connection with those of 2-(2'-Pyridyl)pyrolle and 2-Pyridyl hydrazine show that nitrogen and carbon atoms are interchangeable, and that coordinate bonds are interchangeable with normal valences with regard to strain, differing only in the source of the shared electrons.



a,a' Dipyridyl complex



α',α' Phenanthroline complex



Ferrous 2-Pyridyl hydrazine

Substitution in the aromatic ring as in the following compounds, however, inhibits the reaction (12):

6,6'-dimethyl-2,2'-dipyridyl | 6,6'-diamino-2,2'-dipyridyl | 2(2-pyridyl) quinoline

Organic amines such as ethylene diamine combine with cobalt ion to saturate the coordinate valences and form a chelate compound. Each cobalt atom adds three molecules, each containing two nitfogen atoms, and each of these nitrogen atoms donates one pair of electrons. (8, p. 22).

Feigl(12) also lists the potassium xanthate reaction for molybdenum, giving $MoO_3(SC(SH)(OC_2H_5))_2$, and the identification of sodium as sodium zinc uranyl acetate, $(NaZn(UO_2)_3(CH_3COO)_9.9H_2O$, as examples in which an organic reagent functions as a neutral constituent.

Another coordinate addition product is the water-insoluble complex formed by b-naphthoquinoline with cadmium in the presence of soluble iodide. The metal coordinates with the cyclic tertiary nitrogen atom of the reagent molecule (24).

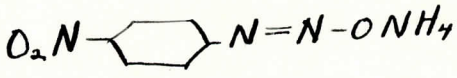
Pyridine, because of the residual valences of its cyclic tertiary amino group forms metallic addition products, water-insoluble and colored.

Two molecules of allyl iodide hexamine, a double salt of hexamethylenetetramine and allyl iodide, coordinate with metals such as cadmium in neutral solution.

Frere (15) has shown that the thorium and uranium salts of oxine form addition compounds with an additional mol of 8-hydroxyquinoline.

Normal Salt Formation

Ammonium ion may be identified by the reaction with p-nitrodiazobenzene in the presence of alkali to the give the redsalt:

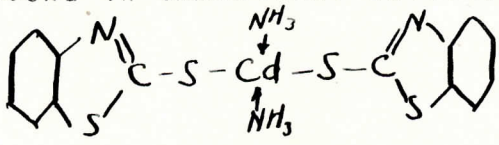


The biuret reaction is another example, in which a red color is produced by salt formation between copper and two $CONH_2$ groups.

Calcium forms yellow insoluble normal salts with the sodium salt of dihydroxytartaric osazone. Zinc and other metals act similiarly and interfere with this test.

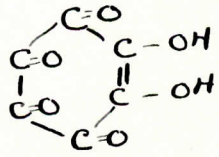
Oxalates are commonly used for precipitations of metals, involving only an ordinary metathesis reaction.

b-Mercaptobenzothiazole forms a somewhat unusual insoluble cadmium compound in ammoniacal solution:

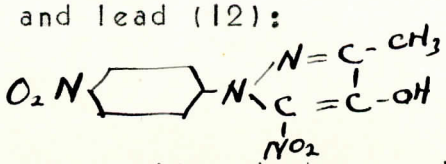


The ammonia is said to be driven off by heating.

Rhodizonic acid determines barium and strontium in the presence of magnesium and the alkali metals (12):



Picrolonic acid is used for gravimetric determination of potassium, calcium, thorium and lead (12):



Some of the hydroxy-oximes mentioned above act as dibasic acids.

Adsorption Phenomena

Combination of metallic ions or other units with organic molecules may take place in non-stoichiometric ratios, as a result of surface energy. It is often very difficult to determine whether a reaction product is of this nature or forms a true compound.

Langmuir in his study of surface chemistry (21a) lists the binding forces which are operative both at the surface and in the interior of particles, and to each of which there should be a corresponding type of adsorption.

(1) Coulomb forces between ions or ions and electrons, varying as $1/r^2$, characteristic of salt-like substances.

(2) Forces between dipoles, varying as $1/r^4$, and depending upon the orientation of the dipoles.

(3) Valence forces associated with the sharing of electrons between atoms.

(4) Van der Waals attractive forces which depend upon the mutual polarizability of molecules, usually varying as $1/r^7$.

(5) Repulsive forces due to the mutual impenetrability of completed electronic shells.

(6) Electron pressures of the Fermi electron gas as in the alkali metals.

Forces such as (2) and (4) lead to adsorption, on the surface of molecules, of other particles. Surface energy is a contributing factor, and adsorption is affected by particle size and surface area. Concentration, temperature and pressure are also determinatory.

Mellan quotes the findings of Weiser and Porter with respect to certain addition products which have been presented as complexes

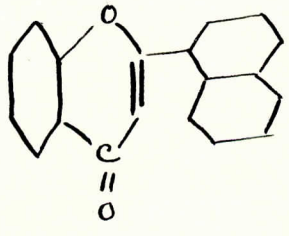
of definite structure, but which they believe to be adsorption products. The studied the relations of both acid and basic dyes with the hydroxides of iron, chromium, and aluminum, and could find no indication of a definite chemical compound at any pH.

Alizarin lake formation is thus believed by some authorities to be due to adsorption of the anion of the dye by the insoluble hydroxide. While some may be chemically combined, most of it is held on the surface of the precipitated particles in non-stoichiometric ratio. Other reagents believed to behave similiarly are morin, aurintricarboxylic acid, tannin and titan yellow.

Tannin precipitates Fe, Al, Cr, Sn, Zr, Ti, and Th in acetic acid solution and W in sulfuric acid. The mechanisms are thought to be adsorption compounds of tannin with the hydrolysis products of the salts.

Magnesium reacts with titan yellow to give a red color, thought to be due to adsorption of the dyestuff on the hydroxide (35). Aluminum gives a positive interference, probably reacting through the same mechanism.

The iodine-starch reaction is an example of adsorption. Similiar is the the action of iodine or bromine on a-naphthoflavone:



-II-

On the following pages there are presented discussions of several tests for metallic ions in qualitative analysis. Experimental results are given on a number of tests for the metals aluminum, cadmium, cobalt and zinc, together with a few miscellaneous reagents which it was thought might be of use.

Studies were made of sensitivity and interferences. Not only is it necessary for the analyst to know what ions interfere with a given test, but it is advantageous to have available information as to the nature of the interference: that is, whether it is positive, the interfering ion giving a false test for the ion sought, or whether it is negative, the interfering ion repressing or inhibiting the desired reaction. Also in the case of color reactions, it is helpful to know the other colors produced by interfering substances.

Solutions of the nitrates of the metals, unless otherwise indicated, made up to contain 10 mg. of metal per cc. were used. In the dilution tests for sensitivity these were taken in the ratio with water specified.

Abbreviations:

c- color
ppt.- precipitate
\+ - positive interference
\- - negative interference
0 - no effect or result.

Alizarin — Test for Aluminum

1,2-dihydroxyanthraquinone — The reagent is soluble in acetic acid, alkali solution, benzene, carbon disulfide, alcohol, ether, and water. A red color is formed with aluminum, in slightly basic solution. It was found however, that both NaOH and NH_3 react with the reagent to give a reddish purple precipitate which may be deceptive. Therefore it was found advantageous to take a portion of the reagent solution before use and add NH_3 until the purple precipitate just disappeared on stirring; this solution was then used as reagent.

Experimental Results- Three drops of aluminum solution were placed on a spot plate, and two drops of reagent added. It was found that comparison with a blank was necessary. The reagent was a saturated acetic acid solution, treated as described above.

Sensitivity- 1/100 Satisfactory.
1/1000 Just noticeable red tinge.

Interferences:	Ion alone	Ion plus Al^{+++} 1:1
Fe^{+++}	Ppt. of hydroxide	Positive
Cu^{++}	Blue ppt.	Combines preferentially
Ba	Orange ppt.	Some + interfer., no −.
Ni	Light violet ppt.	Satisfactory
Ag	Brownish ppt.	"
Co	Dark pink c. or ppt.	Color of solution interferes
Cd	Yellowish turbidity*	Satisfactory
Sr	"	"
NH_4NO_3	"	"
Zn	"	"
$NaNO_3$	"	"
Na_2CO_3	"	"
Mg	"	"
KNO_3	"	"
Pb	"	"

(* Same as blank)

Remarks- According to Mellan, Cr, Fe, Mn, Th, Ti, and U interfere. He calls for carrying out the test on filter paper with exposure to ammonia fumes after adding the reagent, but this was found to give the false purplish-red color. Other interferences may be removed by adding a mixture of ammonium thiocyanate-barium nitrate, or by precipitation with ferrocyanide.

In alkaline solution precipitates are said to be formed with Al, Sb, Bi, Co, Cu, Fe(ous), Mg, Hg (ic), Pt, Sn, Cd, Sn-Red; and with Cd, Sn(ic)-Orange; and with Fe(ic), and Ti-Black; with Cr, yellow; with U-violet; Tl, dark blue. (24, 6)

Aluminon Test for Aluminum

Ammonium salt of aurintricarboxylic acid. Soluble in water.

Forms a red color with aluminum.

Experimental Results- Reaction was carried out in semi-micro test tube using a neutral solution. It was found that either acid or basic solutions of any appreciable concentration give a red color with the reagent. Two drops of the reagent were added to 1 cc. standard solution.

Sensitivity 1/100 Satisfactory.
1/1000 Barely noticeable tint.
1/10,000 Barely distinguishable from blank.

Interferences:

Co	Much pink ppt., and pink c.
Mg	Reddish color
Na	O
Cd	Pinkish white ppt.
Cu	Ppt. whitish brown-gray-dark red.
K	O
Ag	White ppt. faintly gray-brown.
Zn	Pinkish-white ppt.
Na_2CO_3	O
Ba	O
Sr	O
Ni	Whitish ppt., turning pink.
Fe^{+++}	Deep reddish-purple ppt.
Pb	Brownish white ppt.
NH_4NO_3	O

Remarks- The usual qualitative procedure calls for addition of ammonium hydroxide and ammonium carbonate to adjust adidity and dissolve some of the interfering lakes, including Cr. The lake of Al will not form in alkaline solution in the presence of NH_3, particularly. PO_4 interferes negatively and together with iron must be removed. Roller recommends the use of acetate buffer, which gives greater sensitivity and at the same time makes possible accurate colorimetric comparison. (17, 24, 27).

Morin — Test for Aluminum

3,5,7,2',4'-pentahydroxyflavone Soluble in acetic acid, alkalies, and EtOH. Reacts with aluminum in neutral or acetic acid medium to form a green fluorescent soluble complex.

Experimental Results- Saturated solution in EtOH was used, and reaction was carried out on spot plate. Several drops acetic acid and one drop only of reagent were added. It was found that the order of addition of these two made little difference, that the acetic acid helped to remove the brown color of the reagent solution and that two drops of reagent in the spot depression gave too much brown color.

Sensitivity- 1/100 Almost as strong test as full strength.
1/10,000 Apparent alone, positively confirmable by blank.

Interferences-

Mg	O
Na	O
Cd	O
Cu	Green color in solution.
Ag	O
Sr	O
Ba	O
Ni	Green solution.
Fe^{++}	Dark brown color, solution almost opaque.
Co	O (Color of ion)
Pb	Slight greenish yellow color
NH_4NO_3	O
K	O
Zn	Slight yellow color
Na_2CO_3	O

Remarks- Mellan states that gallium, indium, and scandium (in the same periodic group) give the same reaction. Although this seems to be a quite satisfactory test, sufficiently sensitive, and without serious interference other than colored ions, there does not seem to be much available information. (24)

Pyridine-Thiocyanate — Test for Cadmium

These reagents, separately and together, precipitate a numbermof metals. Experimental results were obtained as follows:

Ion	+ KCNS	+ CNS+pyridine	+ pyridine
Fe^{+++}	Deep red	Orange ppt	Orange ppt.
Cd	O	Much white finely divided ppt.	O
Ag	White ppt.	No change	O
Ba	O	O	Slight turbidity
Al	O	White gelat. ppt.	White gelat. ppt.
Ni	O	Same as Cd	Sol. turns blue
Cu	Yellow-green sol.	Yellow green ppt.	Deep blue colored sol.
Sr	O	O	O
Co	O	White ppt.	O
NH_4NO_3	O	O	O
Zn	O	White ppt.	O
Pb	O	"	O(slight turbidity)
Mg	O	O	O
Na_2CO_3	O	O	O
K	O	O	O

a-Nitroso-b-naphthol — Test for Cobalt

Reagent is soluble in benzene, hot EtOH, ether, acetic acid.

A brown color or ppt. is formed with cobalt in acid solution.

The reagent loses its effectiveness upon standing in solution.

Experimental Results- Saturated solution in 50% acetic acid was used. Reactions were carried out in semi-micro test tubes. It was found desirable to compare with a blank in some cases, and also it was found that the color develops somewhat slowly. Nitric acid produces a false red color.
Sensitivity- 1/1000 Quite satisfactory ppt.
1/10,000 gave no effect.

Interferences-	Ion alone					Ion plus Co
	HAc	H_2SO_4	NH_3	NaOH	Neutral HNO_3 added	
Co	Red-br. ppt.	Red-br. c.	Red-br. ppt.	Red-br. ppt.	Red ppt.	-
Fe^{+++}	"	"	"	"	" Color destroyed	None with HNO_3
Ni	Yellow c.	Yell.C.	Yell.C.	Yell.c.	Yell. c *	No. inf.
Al			Same			
Ag			Same			
Ba			Same			
Cd			Same			
Mg			Same			
NH_4NO_3			Same			
Sr^4			Same			
Zn			Same			
Pb			Same			
Na_2CO_3			Same			
KNO3			Same			
Cu	Dark yel. c.	"	Deep gr. c.-decol. by nitric acid.	"	Dark yell. c.	* Appears to combine preferentially when amt. Co is small

* HNO_3 bleaches the NH_3 sol., but makes the neutral sol. turn red, without the characteristic turbidity or ppt., however.

Remarks- Mellan: In a slightly acid medium forms colored complex ppts. with Bi, Cr, Co, Cu, Fe, Pd, Ag, Sn, Ti, W, U, V, Zr ions. Ammonium citrate removes interference of Al, Cr, and Fe. Cu, Mn and Ni must be removed. (24). *Boiling with HNO_3 destroys Fe^{+++} lake.*

Dimethylglyoxime — Test for Cobalt

Reagent gives red precipitate with nickel and brown color with cobalt.

Experimental Results- 0.5 cc reagent was added to one cc. solution, followed by .2cc. o-toluidine solution. Organic amines increase the sensitivity of the test.

Sensitivity- Without o-toluidine, only 1/100 was detectable; with it 1/1000.

Interferences-

	HAc	H_2SO_4	NH_3	NaOH	HNO_3	Neut.	Interf.
Co	Brown	pink	brown	brown ppt.	pink	Intense red-br. c.	-
Fe	"	yellow	(ppt.)	(ppt.)	yellow	Red	+ in alk.
Ni	Red ppt.	O	red ppt.	red ppt.	O	Red ppt.	Preferentially reacts.
Al	O	white ppt.	-	-	O	O	None
Ba	O	-	O	white ppt.	white	O	None
Cu	Brown c.	O	br. c.	br. c	br. c.	br. c.	+
Ag	Faint white ppt		-		O	Faint ppt.	None
Cd			O				None
Sr			O				None
Zn			O				None
Na_2CO_3			O				None
Mg			O				None
K,			O				None
Na			O				None
Pb			O				None

Scott (30) and Braley and Hobart (4) give good discussions of this test and its applications. Dichl (10) considers it in detail.

Nitroso-R-Salt — Test for Cobalt

Disodium salt of 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate.

Reagent is soluble in water. Yields a red color or precipitate with cobalt.

Experimental Results- 0.5% aqueous solution was used. Reactions were carried out in semiemicro test tubes. ½cc. reagent was added to 1 cc. solution.
Sensitivity- 1/100 strong red.
1/1000 moderately red.
1/10,000 no result.

Interferences-

	Neutral	HNO_3	NH_3	HAc	H_2SO_4	NaOH	+ Co
Co	Red c.	O	Br. ppt.	O	O	Br. ppt.	-
Fe^{+++}	"	O	"	O	O	"	+, destroyed by nitric acid.
Ni	O	O	O	O	O	Yell-Br. ppt.	Seems to inhibit reaction.
Al	O	O	O	O	O	O	None
Ag			Same				
Ba			Same				
Sr			Same				
Na_2CO_3			Same				None with HNO_3
Cd			Same				
Mg			Same				
K			Same				
Pb			Same				
Zn			Same				
Cu^{++}	Br.-yell. c.	Yell.gr. c.	Ppt. then deep gr. sol.	O	O	Green ppt.	None with HNO_3

Remarks- Mellan says the following precipitates are produced: Ba-orange; Ca-green; Co-deep red, Fe^{++}-green; lead-red; Ni- yellow brown; Ag-lemon yellow. Colors produced by iron, nickel, copper and other metals are destroyed by nitric acid, while that of cobalt is not. High concentrations of colored ions interfere. The reagent is more stable than a-nitroso-b-naphthol and according to van Klooster does not itself precipitate.

Resorcinol — Test for Zinc

Yields a blue color with zinc in ammonia solution, turning to an orange-red color in acid.

Experimental Results-
5% aqueous solution was used. 3 drops reagent and 5 drops ammonia were added to $\frac{1}{2}$ cc. solution in test tube and allowed to stand for about five minutes. There was considerable time lag in the development of color.
Sensitivity- 1/100 was greatest dilution which gave a test. Blank tends to turn green also; comparison should be made.
Interferences-

Zn- dark blue color, quite transparent; acidification converts to light salmon.
Cu- dark brownish blue color; acid- light yellow-green.
Fe- deep purplish color before add. of NH_3. Acidification removes this.
Cd- green to blue; salmon in acid.
Ni- blue; bleached in acid.
Pb- white ppt plus blue sol.; same in acid.
Ba- slight green color.
Ag- yellow-green, turning pink in acid.
Sr- yellow-green, nothing in acid.
NH_4NO_3- Same
Na_2CO_3- Same
Co- brown sol; salmon in acid.
Mg- O
Na- O
K- O
Al- hydroxide is precipitated slightly brown.

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